



**Agricultural
Research
Service**

**United States
Department of
Agriculture**

National Sedimentation Laboratory

Oxford, Mississippi 38655

GROUND WATER RESEARCH

**RESEARCH PROGRESS REPORT
1990/991**

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Technology Application Project Report No. 18

SEPTEMBER 1992

P.C. #8107

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FORWARD AND EXECUTIVE SUMMARY

Maintaining and/or improving crop production efficiency without adversely affecting environmental quality is a major challenge for U. S. agriculture. Pesticide and nitrate-N contamination of ground water is a critical problem that needs timely and rational solutions. There is a great public concern about ground water quality since it is the source of drinking water for half of the U. S. In rural communities nearly 95% of the population depends upon wells for drinking water.

As part of the Interagency Demonstration Erosion Control Project (DEC) in the Yazoo Basin, northern Mississippi, the USDA National Sedimentation Laboratory, Erosion Processes Research Unit, initiated a study of cost - effective practices for control of upland erosion on the Ed Nelson Farm located in Tate County, Mississippi. During 1989 this research was expanded by the Water Quality/Ecology Research Unit to include water quality studies of shallow ground water and surface runoff. Perched ground water (0.5 to 10 feet) and surface runoff from a no-till and a conventional-till watershed are sampled and analyzed for pesticides and plant nutrients.

The research reported here places an emphasis on the effects of conservation tillage practices on ground and surface water quality, with the objective to develop economically and environmentally sound crop production systems. It has been estimated that between 60 - 70% of all U. S. cropland will employ some type of conservation tillage by the year 2000. For much farm land, conservation tillage is the only way to reduce soil erosion to acceptable limits as provided by the Food Security Act of 1985. While conservation tillage minimizes nonpoint contamination of surface water by reductions in runoff and erosion, it also increases infiltration, and hence, the potential for increased leaching of pesticides and fertilizers. The results within this report represent only two years of research and should be considered preliminary. They do, however, provide the following insights on the quality of ground and surface water of a no-till and conventional-till soybean watershed:

1. Free water is easily perched above the fragipan during wet seasons, and is suspected to move down slope across the fragipan surface.
2. Tillage differences between no- or conventional-till systems, do not appear to affect the concentration of nutrients in shallow ground water.
3. Even though no N was applied to soybeans, shallow ground water at times exceeded U. S. Drinking Water N standards. Crop residues are suspected as the N source.
4. Riparian zones below agricultural areas may serve to reduce nitrate-N content in ground water.

5. Herbicide losses in runoff were primarily dependent on the amount of runoff in the first runoff event after application and were independent of established tillage practices. However, no-till reduced sediment loss by about two orders of magnitude compared to conventional tillage.
6. Substantial herbicide losses in runoff (as much as 10 - 20%) resulted when 35 mm or more of runoff occurred within 1 week of broadcast (surface) applications of relatively water soluble herbicides such as metribuzin and metolachlor.
7. The no-till practice provided a greater potential for herbicide and nitrate-N leaching into the soil profile.
8. Models used to predict the mass balance using only the matrix (Darcian) flow will underestimate those chemicals like bromide that move into the soil profile.

These research projects are designed to last several years so that a range in environmental conditions will make the results more reliable. Also, the data will require more analysis before formal publication.

The scientists wish to acknowledge the technical assistance and quality service of Kenneth Dalton, Steve Smith, James Hill, Edward Gurley, Tommy Winter, Alan Hudspeth, Blake Sheffield, and Matt Gray. We especially thank Earl Grissinger, Carl Murphree, and Seth Dabney of the Erosion Processes Research Unit at the National Sedimentation Laboratory, and Charlie Cooper, Research Leader of the Water Quality and Ecology Research Unit.

We also appreciate the assistance of our cooperators in these projects - Mr. Bill Lipe of the Soil Conservation Service, and Drs. Joe Johnson, Joe Sanford, and Glover Triplett of the Mississippi Agricultural and Forestry Experiment Station.

GROUND AND SURFACE WATER QUALITY RESEARCH IN THE LOESS/FRAGIPAN SOILS OF NORTH MISSISSIPPI¹

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I. INTRODUCTION

The Agricultural Research Service of the USDA has a ground and surface water quality protection program in which the general goal is to "assess what effect agriculture has on water quality and develop new agricultural management practices and systems that are cost effective and will protect and enhance water quality" (U. S. Department of Agriculture, 1991). There is increased emphasis on our understanding of the fate and transport of agrochemicals in agricultural ecosystems. Another research emphasis area is the evaluation and optimization of no-till and other conservation tillage and residue management systems which increase soil organic matter, infiltration, and soil biological activity and reduce runoff and erosion while controlling agrochemical buildup in ground water.

By the year 2000, about 60-70% of all U. S. cropland will employ some type of conservation tillage. For much farm land, conservation tillage may be the only way to reduce soil erosion to acceptable limits as provided by the Food Security Act of 1985. Conservation tillage has proven to minimize nonpoint contamination of surface water by reductions in runoff and erosion, but it also increases infiltration, and hence the potential for increased leaching of pesticides and fertilizers.

The relationships between agricultural practices and ground-water quality have not been addressed as extensively or effectively as have other pollution processes. For instance, tillage practices can have a profound effect on the amount and transport mechanism of pesticides through the soil profile (Kanwar *et al.*, 1985). Minimum tillage practices leave a greater percentage of residue than conventional tillage practices, leave the structure of surface soils largely intact. They also yield more continuous macropores caused by earthworms and aging, reduce soil erosion and surface runoff, and increase infiltration. In contrast, conventional tillage practices, which include plowing, disking, and harrowing, destroy most of the preferential flow paths and reduce the number of pathways for water to move by gravity into the soil profile, increase soil erosion, and increase surface runoff. Limited field studies have been conducted on the transport of chemical pollutants from the soil surface to the ground water in warm surface zones. Preferential paths of water movement and

¹ Mention of pesticides in this paper does not constitute a recommendation for use by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement of preferential treatment by the U. S. Department of Agriculture.

subsequent pesticide and nutrient movement in relation to tillage practices in the southeast region of the U.S. need to be studied because the soils are characterized by warm temperature and medium to heavy textured soil. Fundamental controlled research is also needed to separate the water reaching a subsurface drain during rainfall simulation into its matrix and macropore components. Once the magnitudes of the two flow components were estimated, the relative importance of each in solute transport can be assessed.

Information about the effects of conservation tillage practices on ground and surface water quality is lacking for most of Mississippi, particularly the loessial uplands in the northern part of the state. This paper discusses the USDA-National Sedimentation Laboratory's continuing efforts in this important research area and presents some of the findings to date regarding ground water movement, pesticide, and nutrient transport.

II. MATERIALS AND METHODS

The study was conducted on the Nelson Research Farm located in the loessial uplands of northern Mississippi in Tate county near the town of Como. The fragipan soils are of the Grenada, Loring, and Memphis series. Runoff and shallow ground water sampling sites were established on a 2.14-ha watershed (WSHD 1) in the fall of 1989 and on an adjacent 2.10-ha watershed (WSHD 2) in the fall of 1990 (Figure 1). Each watershed had a mean slope of about 4% and had been in minimum-till soybeans during 1988 and 1989. Each runoff sampling site was instrumented for automatic data and discharge-weighted composite sample collection as described in detail by Grissinger and Murphree (1991) and Cullum et al. (1991). Three shallow ground water sampling sites were located along one edge of each watershed to minimize disturbance to the watershed via foot traffic during sampling (Figure 1). Detailed descriptions of the ground water sampling sites and of the runoff and ground water sampling and handling procedures were reported previously (Smith et al., 1991).

Prior to plant nutrient analysis, all samples were filtered using a 0.45 μm Millipore filter. Runoff and ground water samples were analyzed for $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ using a Dionex HPLC equipped with an AS4A anion column, an anion micromembrane suppressor, and a conductivity detector. Samples were analyzed for $\text{NH}_4\text{-N}$ using the automated colorimetric phenate method (Technicon, 1973).

Pesticide analyses of soil, sediment, and water were also conducted as previously reported (Smith et al., 1991), with the following exceptions. The gas chromatographs were equipped with Dynatech Precision GC-411V autosamplers to facilitate unattended injection of samples. A PE Nelson 2700 chromatography data system, consisting of three model 970 interfaces, Turbochrom 3 software, and a microcomputer with color printer, was used for automated quantification and

reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample. Limits of detection were 0.05-0.5 ppb depending upon the pesticide.

In May 1990 and 1991, metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one, Lexone™) at 0.42 kg/ha and metolachlor [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluidide, Dual™] at 2.24 kg/ha were broadcast applied by ground equipment to each watershed for preemergence weed control. In late May fertilizer (0-20-20) was also broadcasted at 224 kg/ha in 1990 and at 280 kg/ha in 1991. Also in late May both years, WSHD 1 was no-till planted in soybeans [*Glycine max* (L.) Merr., Delta Pine 415] at 50-56 kg/ha. WSHD 2 was conventionally tilled both years just prior to soybean planting (same rate as WSHD 1). In mid-June of both years, each watershed was treated with a broadcast application of acifluorfen-sodium [sodium 5-(2-chloro- α,α,α -trifluoro-*p*-tolylloxy)-2-nitrobenzoate, Blazer™] at 0.28 kg/ha and bentazon [3-isopropyl-(1*H*)-benzo-2,1,3-thiadiazin-4-one 2,2-dioxide, Basagran™] at 0.56 kg/ha for postemergence weed control and with chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate, Lorsban™) at 0.56 kg/ha for soil insect control. Sampling instrumentation was covered during pesticide and fertilizer applications. Aliquots of all spray tank mixes were obtained for confirmation of pesticide application rates.

At the North Mississippi Branch Experiment Station (MAFES) near Holly Springs, Mississippi, potassium bromide (KBr) was used as a tracer in water applied as simulated rain to 1-m² field plots with subsurface drains installed 0.6-m below the soil surface. The plots represented undisturbed pasture and simulated-till conditions and two procedures of installing field drains (horizontal drilling and trenching). Bromide was determined using a Dionex HPLC.

A hydrograph-separation technique (Everts and Kanwar, 1990), using a mass balance and a dual porosity model, was applied to the tracer concentration and flow rate of drainage water to estimate the preferential flow and matrix flow components of subsurface drainage. Individual hydrographs of both matrix and preferential flow were constructed.

The methods of this experiment were based on using a mass balance equation that describes the transport of a solute to subsurface drain flow where:

$$Q_T * C_T = Q_D * C_D + Q_P * C_P \quad (1)$$

Q_T = Total flow rate of drainage in the drain,

Q_D = Darcian flow rate,

Q_P = Preferential flow rate,

C_T = Tracer concentration in drain water,

C_D = Tracer concentration of Darcian flow component reaching drain,

C_P = Tracer concentration of preferential flow component reaching drain.

$$\text{Conservation of mass yields: } Q_T = Q_D + Q_P. \quad (2)$$

By substituting Eq. 2 into Eq. 1, relationships of preferential flow and Darcian (matrix) flow are ascertained:

$$Q_P = Q_T * (C_T - C_D)/(C_P - C_D), \quad (3)$$

$$Q_D = Q_T * (C_T - C_P)/(C_D - C_P). \quad (4)$$

Initially C_P is assumed equal to the concentration of the tracer applied in the rainfall simulation and C_D is the concentration of tracer reaching the drain that increases linearly between the initial value for C_D and the ultimate concentration for C_D at the end of simulation ($C_T = C_D$). These assumptions produced two equations with two unknowns after measuring C_T with respect to time.

At the North Mississippi Experiment Station near Holly Springs, Mississippi, four 1-m² hydrologically isolated plots with drains at fragipan depth were installed. These plots had been in native grass since 1989. A rainfall simulator was used to apply a batch mixture of KBr at 250 mg Br⁻/L on the two plots where the drains were installed from the surface (trenched) and from the side (horizontally drilled). The simulation began after plots reached field capacity as determined through time domain reflectometry procedures when the soil profile was at 32% moisture. The simulations were conducted on undisturbed plots with residues removed (no-till) and disturbed plots shaped by tilling the top six inches of surface soil (conventional-till). The experimental design consisted of two tillages (conventional- and no-till), two simulations approximately 24 hours apart, and two replications. Application of 63.5 mm and 38 mm of water solution was delivered to the plots at 12.7 mm/hr for the first and second simulations, respectively. Type of data collected included measurement of subsurface drain flow and Br⁻ analysis of the flow at intervals during and after the two rainfall simulations.

III. RESULTS

A. Plant Nutrients and Water Quality - J. D. Schreiber

1. Nutrients in surface runoff

The mean discharge-weighted concentrations of PO₄-P, NH₄-N, NO₃-N, Cl, and SO₄-S in runoff from the no-till soybean watershed for the 1991 WY were 0.55, 0.24, 0.64, 1.73, and 0.85 mg/L, respectively, compared with 0.09, 0.12, 0.53, 2.24, and 0.99 mg/L, respectively, from the conventional-till watershed. The generally higher nutrient concentrations in runoff from

the no-till watershed are most likely due to the leaching of accumulated soybean and weed residues. Only the distribution functions of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations differed significantly between the two tillage systems. Soluble $\text{PO}_4\text{-P}$ concentrations in runoff from the no-till soybean watershed exceeded those from the conventional-till by a factor of six. The much higher suspended sediment in runoff from the conventional-till watershed would sorb soluble phosphorus thereby reducing $\text{PO}_4\text{-P}$ concentrations in runoff. For the WY, the mean discharge-weighted suspended sediment concentrations in runoff from the no- and conventional-till watersheds were 67 and 3,569 mg/L, respectively.

Total solution losses of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl, and $\text{SO}_4\text{-S}$ from the no-till watershed for the WY were 3.80, 1.63, 4.39, 11.84, and 5.82 kg/ha, respectively, compared with 0.80, 1.11, 4.72, 19.96, and 8.78 kg/ha, respectively, from the conventional soybean watershed. Only the distribution functions of $\text{PO}_4\text{-P}$ yields differed significantly between the two tillage systems. Total runoff was 690 and 900 mm from the no- and conventional-till soybean watersheds, respectively. Despite lower runoff from the no-till watershed, the soluble $\text{PO}_4\text{-P}$ yield for the WY was nearly five times that of the conventional-till watershed due to the much higher concentrations of soluble $\text{PO}_4\text{-P}$. In a 1990 study (Schreiber et al., 1991) soluble $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl, and $\text{SO}_4\text{-S}$ losses from the same no-till watershed discussed here were 1.21, 0.54, 1.06, 4.98, and 2.21 kg/ha, respectively. Other water quality research in north Mississippi has shown total N and P losses (solution plus sediment) from no-till soybeans at 4.7 and 2.8 kg/ha, respectively (McDowell and McGregor, 1980).

Cumulative frequency distributions of runoff and $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ losses provided additional information on the losses in runoff. For example, considering $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ for the no-till soybeans, 16, 39, and 11 percent of the runoff, respectively, had concentrations that exceeded the discharge-weighted mean concentration and produced about 53, 72, and 58 percent of the losses. Similarly for the conventional-till watershed, 42, 45, and 12 percent of the runoff exceeded the discharge-weighted mean concentrations of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ and produced about 67, 68, and 50 percent of the losses, respectively. In addition, single storm events can contribute a significant portion of the total yearly losses. For the no-till watershed, the three largest nutrient yielding storms represented about 42, 42, and 57 percent, respectively, of total solution $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ losses compared with 45, 53, and 49 percent, respectively, for the conventional-till watershed.

In general, plant nutrient concentrations in runoff showed similar seasonal variations for both the no-till and conventional-till watersheds (Figures 2 and

3). Lowest nutrient concentrations in runoff were observed during the winter and early spring months, a time period of minimal microbiological activity. Low microbiological activity could be expected to decrease soluble nutrient concentrations. The highest $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ concentrations in runoff from the no-till watershed were 22.97, 1.36, and 6.25 mg/L compared with 5.97, 1.77, and 7.21 mg/L for the conventional-till watershed. These high nutrient concentrations are attributed to a broadcast application of 0-20-20 on May 14, 1991. The high $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ concentrations were observed in runoff within two days after fertilizer application, whereas, the higher $\text{NO}_3\text{-N}$ concentrations were not observed until about one month later in runoff from the no-till watershed, and two months later in runoff from the conventional-till watershed. As the fertilizer should not have contained any nitrogen compounds, the increase in $\text{NO}_3\text{-N}$ may have resulted from a stimulation of microbiological activity. During the late spring and summer months $\text{PO}_4\text{-P}$ concentrations rapidly decreased to near pre-fertilization levels. Nitrate-N and $\text{NH}_4\text{-N}$ concentrations also decreased during the summer months but at a slower rate. Nutrient concentrations in runoff, particularly from the no-till watershed, increased slightly during the fall and probably represent leaching of crop residues and desiccated vegetation.

Most likely, solution losses of nutrients from the no-till watershed represented almost all of the total nutrient losses since sediment concentrations and yields were low. For the 1991 WY the mean discharge-weighted sediment concentration in runoff was only 67 mg/L; sediment yield was 455 kg/ha. In contrast, the mean discharge-weighted sediment concentration in runoff from the conventional-till watershed was 3,569 mg/L and a sediment yield of 31,928 kg/ha. More than likely sediment-associated nutrient losses are a substantial portion of the total (aqueous plus sediment) nutrient yield from the conventional-till watershed. Sediments from the individual storms for each watershed are currently being analyzed for N and P content with results to be reported in a separate manuscript.

2. Nutrients in shallow ground water

Ground water samples were first obtained at the beginning of December from the no-till watershed after a total of 191 mm of rain fell from the start of the 1991 WY. In contrast, it took an additional 197 mm of rainfall before shallow ground water was present in the observation wells of the conventional-till watershed, about the middle of December. In addition, during the WY, 169 samples were obtained from observation wells of the no-till watershed compared with only 86 samples for the conventional-till watershed. Greater infiltration is thought to be one factor for the larger

abundance of shallow ground water in the soil profile of the no-till watershed. A typical distribution of water in the observation wells for both watersheds after a storm event is shown in Figure 4. These data show the tendency of ground water to pond above and within the fragipan located 0.61 to 0.91 m below the soil surface. The data also indicate an abundance of ground water within the fragipan itself. Research has indicated that a common characteristic of fragipan soils is that the material above the fragipan is usually quite porous whereas the fragipans have a much lower saturated hydraulic conductivity than the materials above, hence, low tension water accumulates at the top of the fragipan and moves laterally (Grossman and Carlisle, 1969; Römken et al., 1986).

The 1991 WY annual mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ concentrations for all ground water sites and depths of the no-till watershed were 0.06, 0.10, 4.50, 11.94, and 2.38 mg/L, respectively, compared with 0.04, 0.11, 5.83, 12.18, and 1.97 mg/L, respectively, for the conventional-till watershed. Despite similar mean nutrient concentrations, only the distribution functions of $\text{NH}_4\text{-N}$ concentrations for all sites and depths were statistically the same (5 percent level). As expected, with the exception of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$, nutrient concentrations in ground water were higher than those in runoff. For the WY only a relatively few shallow ground water $\text{NO}_3\text{-N}$ concentrations from either watershed exceeded the U.S. Drinking Water Standard of 10 mg/L. Only 3 (5 observations) and 2 (2 observations) percent of all $\text{NO}_3\text{-N}$ concentrations from the no-till and conventional-till watersheds, respectively, exceeded the standard. In contrast, during the 1990 WY (Schreiber et al., 1991) 59 percent of all $\text{NO}_3\text{-N}$ concentrations of the no-till watershed exceeded the nitrate-N standard. Continued $\text{NO}_3\text{-N}$ leaching from the soil profile by a higher than normal rainfall during the 1991 WY is probably the main reason for decreased $\text{NO}_3\text{-N}$ concentrations in ground water. Total precipitation for the 1991 WY was 1,783 mm, 34 percent greater than the 30-year mean. No N fertilizers have been added to these watersheds since 1987. In contrast to the watersheds, $\text{NO}_3\text{-N}$ concentrations in ground water from a riparian zone were much lower.

For all sites and depths, the 1991 WY mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ concentrations in shallow riparian ground water was 0.03, 0.08, 0.38, 2.66, and 4.72 mg/L, respectively. Assuming that ground water within the conventional-till watershed flows downslope across the fragipan surface to the riparian zone, the 93 percent reduction in $\text{NO}_3\text{-N}$ concentration can be attributed to vegetative uptake and/or denitrification. Other research has shown riparian zones to be very effective areas by which to reduce high $\text{NO}_3\text{-N}$ concentrations in agricultural runoff and ground water flow (Jacobs and Gilliam, 1985).

As in other research (Staver and Brinsfield, 1989), it appeared that one of the primary factors that determined the magnitude of N leaching losses to ground water was the availability of soluble N forms, especially nitrate, in the upper soil profile after the soybean harvest. In addition, legumes may cause a greater availability of $\text{NO}_3\text{-N}$ in the root zone and hence can promote significant nitrification and $\text{NO}_3\text{-N}$ leaching (Groffman et al., 1987). Furthermore, the use of conservation tillage may result in increased infiltration rates due primarily to the formation of macropores in the soil, and thus increasing the likelihood of chemicals leaching beyond the root zone (McCormick and Algozin, 1989). Three coastal plain studies indicated that even when recommended nutrient management practices were followed, $\text{NO}_3\text{-N}$ concentrations in shallow ground water were significantly higher than the standard for public drinking water. In one study of conventional-till soybeans, thirty-nine out of forty-four samples exceeded the nitrate-N standard of 10 mg/L (Magette et al., 1989). Ground water at 1.5 m with corn that received N fertilization showed $\text{NO}_3\text{-N}$ concentrations to be about 18 mg/L (Weil et al., 1990). Tile drainage from Ohio alfalfa over a two year period averaged 1.5 mg/L $\text{NO}_3\text{-N}$, compared with 4.9 to 32.8 mg/L measured under soybeans (Logan et al., 1990). In this present study, soybean residues, tops and roots, are suspected as the $\text{NO}_3\text{-N}$ source.

In general, for both the no-till (Figure 5) and conventional-till (Figure 6) watersheds, $\text{NO}_3\text{-N}$ concentrations at all depths were higher during the winter months and decreased during the spring due to 1) continual leaching of the soil profile, 2) nutrient uptake by a prolific late winter-early spring growth of native vegetation, and 3) denitrification. For most sites on both watersheds $\text{NO}_3\text{-N}$ concentrations were higher at the 1.52 m depth compared with shallower depths and may be an indication of $\text{NO}_3\text{-N}$ accumulation with time. Distribution functions of $\text{NO}_3\text{-N}$ concentrations in ground water for the individual storms of both the no- and conventional-till watershed differ significantly (with a few exceptions) at observation well depths 0.61 m or greater, but were similar at well depths 0.46 m or less. Distribution functions of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ concentrations for each watershed were the same across study sites at all well depths. No trends in $\text{PO}_4\text{-P}$ or $\text{NH}_4\text{-N}$ concentrations were observed with season or well depth. Similar observations were made for the no-till watershed during the 1990 WY (Schreiber et al., 1991).

Ground water samples were collected and analyzed from both observation wells and soil water suction tubes, all at the same sites and depths. The annual WY mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl, and $\text{SO}_4\text{-S}$ concentrations in ground water collected by soil water suction tubes from the no-till

watershed were 0.04, 0.07, 3.40, 8.33, and 8.45 mg/L, respectively, compared with 0.04, 0.11, 6.20, 19.43, and 18.77 mg/L, respectively, for the conventional-till watershed. At all sites, for each watershed, for individual storm events, distribution functions of Cl and NO₃-N concentrations, collected by these two techniques, generally differed significantly at depths greater than 0.46 to 0.61 m. The SO₄-S concentrations differed significantly at all depths. In contrast (except for a few depths and sites) PO₄-P and NH₄-N concentration distribution functions did not differ between the two sampling methods.

B. Pesticides and Water Quality - S. Smith, Jr.

1. Pesticides in surface runoff

As reported previously (Smith et al., 1991), only 4 runoff-producing rainfall events occurred during the 1990 crop year, after the preemergence herbicides metribuzin and metolachlor were applied to the no-till watershed and prior to soybean harvest in early October. Metribuzin and metolachlor concentrations in the water phase of runoff were 111 and 535 ppb (µg/L), respectively, 6 d after application (Table 1). By 27 d after application, these values had decreased to <3 ppb; by day 85, the herbicides were almost undetectable. A strikingly similar downward trend in concentrations was observed during crop year 1991 (Table 2). Metribuzin and metolachlor concentrations were 223 and 525 ppb, respectively, 5 d after application (first runoff-producing rainfall) and by day 103, neither herbicide could be detected in runoff water. However, total losses of metribuzin and metolachlor in runoff water during crop year 1991 were about 20 and 9%, respectively, of the amounts applied, or about 5 and 2.5 times the respective losses (about 4% for each herbicide) during crop year 1990. This can be explained by examining the runoff pattern each year. In both years, the first runoff event occurred within 1 w after herbicide application; however, the first runoff volume in 1991 was about 7 times the first runoff in 1990. By the time the second runoff event occurred each year (day 13 in 1990 and day 23 in 1991), less herbicide was available at the soil surface for runoff because of other loss factors such as biodegradation, leaching, and possibly volatilization and photodegradation. Although almost 60 mm runoff occurred in the second event in 1990, the loss was only about 2.5% of that applied for each herbicide.

In crop year 1991, herbicide concentrations and losses in the water phase of runoff from the no-till and conventional-till watersheds were almost the same (Tables 2 & 3). Metribuzin and metolachlor concentrations were highest in the first runoff event (4-5 d after application) and reached levels noted above for the no-till and 241 and 590 ppb for the conventional-till

watershed. Total seasonal losses of the herbicides from the watersheds (20 and 9% metribuzin and metolachlor from the no-till watershed and 23 and 11% from the conventional-till watershed, respectively) were similar also, but higher for the conventional-till watershed by a factor of about 1.2 for each herbicide. Total runoff from the conventional-till watershed (76 mm) during the growing season was greater than that from the no-till watershed (64 mm), also by a factor of about 1.2, accounting for the differences in solution-phase losses of the herbicides from the watersheds.

No metribuzin and metolachlor residues were detected in the sediment phase of runoff from the no-till watershed in either 1990 or 1991 because of the low sediment concentrations in runoff (about 35-550 mg/L, Tables 1 & 2). The relatively low organic carbon partition coefficients (K_{OCs}) and relatively high water solubilities (S_{H_2O} 's) of metribuzin and metolachlor (Figure 7) resulted in these herbicides being transported in runoff almost entirely in the water (solution) phase. Metribuzin and metolachlor residues were detected in the sediment phase of runoff from the conventional-till watershed in 1991, because of the much higher sediment concentrations in runoff (about 7000-55,000 mg/L, Table 4) resulting from tillage operations (cultivations). Highest herbicide concentrations in sediment were about 90 and 312 ppb ($\mu\text{g/kg}$) for metribuzin and metolachlor, respectively, and occurred in the first runoff (4 d after application). Total seasonal herbicide losses in sediment were only 0.1-0.2% of applied and again reflected the strong partitioning of the herbicides toward the solution phase of runoff. The increased sediment concentrations in runoff 22 and 63 d after herbicide application were the result of cultivations in June and July.

No residues of acifluorfen-sodium, bentazon, or chlorpyrifos were detected in runoff from events that occurred after their application in mid-June each year because the compounds were applied at reduced rates and had probably undergone extensive degradation by the time the first runoff event occurred (Smith et al., 1991).

2. Pesticides in shallow ground water

Not all runoff-producing rainfall events produced shallow ground water for sampling as evidenced by the observation well data in Tables 5 & 6 for the no-till watershed in crop years 1990 and 1991, respectively, and in Table 7 for the conventional-till in crop year 1991. Herbicide concentrations in the wells of the no-till watershed (both years) showed that both metribuzin and metolachlor rapidly move downward to the fragipan (about 0.6 m below soil surface) with the first rainfall event after herbicide application. Furthermore, the herbicides penetrated at least 0.9 m into the fragipan,

particularly at site 1 (most upslope site) with concentrations reaching 46 and 151 ppb for metribuzin and 72 and 254 ppb for metolachlor in 1990 and 1991, respectively. Fragipan penetration by water (and solutes) may result from movement into "fingers" (polygonal seams) of more permeable material that naturally occur in the fragipan. Herbicide concentrations in ground water at sites 2 & 3 suggest substantial lateral movement of the herbicides downslope. The data further suggest some herbicide accumulation in the upper part of the fragipan as well as penetration into the fragipan. The other ground water-producing rainfall events in 1990 occurred 13 and 27 d after herbicide application resulting in water in 21 and 15 wells, respectively (Table 5). The rainfall on day 13 (112 mm) occurred only 1 w after the first rainfall, whereas the rainfall on day 27 (26 mm) occurred 2 w after the second rainfall, allowing the soil profile more time to dry between rainfall events. Herbicide concentrations were quite variable and randomly distributed both times from 0.15 m down to 1.5 m. In 1991, the other ground water-producing rainfall event in the no-till watershed occurred 23 d after herbicide application resulting in water in 6 of the 21 wells (Table 6). This second rainfall (59 mm) occurred >2 w after the first rainfall (71 mm), thus allowing the soil profile that time interval to dry. Again, herbicide concentrations were variable, with no distribution pattern evident other than general movement to and into the fragipan.

In 1991, the first ground water-producing rainfall event occurred only 4 d after herbicide application on the conventional-till watershed. The herbicides penetrated the fragipan at the two uppermost sites (1 & 2) but remained above the fragipan at site 3 (Table 7). However, maximum herbicide concentrations found were <9 ppb regardless of depth. The second rainfall event, which produced runoff on both watersheds and ground water in the no-till watershed, failed to produce ground water in any of the wells in the conventional-till watershed.

Herbicide concentrations in shallow ground water decreased rapidly during the growing season. The next ground water-producing rainfall events did not occur until after soybean harvest in October of each year and no herbicides could be detected. Probable contributing factors were rapid herbicide biodegradation (short half-lives, $t_{1/2}$'s in Figure 7), movement of the herbicides out of the watersheds in lateral subsurface flow, and movement of the herbicides deeper into or possibly through the fragipan.

C. Ground Water Movement Research - Preferential Flow - R. F. Cullum

If either preferential or matrix flow were the only mechanism for the transport of solutes to subsurface drainage, the concentration of Br^- in drainage would be expected to increase for as long as the tracer solution was applied or until the

concentration of the tracer in the drainage water reached the same concentration as that applied in the tracer solution. Figure 8 shows Br^- concentrations measured in the drain outflow during the 5-hour simulation event for each treatment. The drain line was not flowing at the start of the simulation but flow began on the average of 50 minutes after irrigation began. During each irrigation, Br^- concentrations in drain outflow reached a peak and then began to decline. A peak in Br^- concentrations occurred between 280 to 300 minutes during the first irrigation. This increasing and decreasing concentration of tracer in drain outflow is consistent with a dual porosity model.

Hydrographs in Figures 9 and 10 are the result of solving Equations 3 and 4 for preferential and matrix flow using the Br^- concentrations in the drainage shown in Figure 8. Figures 9 and 10 show the dominant mechanism for water reaching the subsurface drain line is matrix flow. Matrix flow appears to contribute the majority of the water moving to the drain line even during the early stages of the drain flow hydrographs. Initial mixing between the macropores and matrix flow, combined with high antecedent soil moisture content at the start of the experiment, may explain why macropore flow does not show greater response during the early stages of flow. Figure 11 presents the relative contribution to drain outflow made by preferential flow during the first irrigation for each treatment. The undisturbed plots produced more preferential flow than the simulated-till plots, independent of how the drains were installed.

Total discharge and total mass of Br^- from each rain simulation are shown in Table 8. The undisturbed pasture condition with the horizontal-drilled drains showed preferential flow contributed 31% and 17% of its total discharge from the 5- and 3-hour storms, respectively, while the undisturbed pasture condition with trenched drains showed preferential flow contributed only 16% and 9% of its total discharge for the two respective storms. However, the total discharge from the undisturbed pasture condition was 6% higher for the trenched drains as compared to the horizontal-drilled drains which imply the trench may be inducing significant water movement that is non-representative of the actual water flow patterns for these soils. The simulated-till plots for both drain installation procedures produced preferential discharge of 14% and 25% of the total discharge for the 5- and 3-hour storms, respectively. The simulated-till procedures probably reduced the number of continuous macropores thus causing reduced preferential flows. Even though preferential flow contributed relatively small amounts of total drain outflow as compared to the matrix flow, preferential flow contributed on a mass basis 55% and 18% of the bromide for the 5- and 3-hour storms, respectively, under undisturbed pasture conditions and 28% and 35% of the bromide for the two storms under simulated-till.

IV. CONCLUSIONS

The results presented within this report represent only one to two years of research and should be considered preliminary. They do, however, provide insights regarding the quality of ground and surface water of a no-till and conventional-till soybean watershed. Data indicate that tillage differences, conventional or no-till, do not affect the concentration of plant nutrients in shallow ground water. However, no-till may increase the potential for nutrient movement in ground water. Soluble plant nutrient concentrations and yields in surface runoff from conventional and no-till soybeans are relatively low, and should pose no environmental problem. Even though no nitrogen was applied to the soybeans, shallow ground water at times exceeded U.S. drinking water N standards. Crop residues are the suspected N source. Riparian zones located below agricultural watersheds may serve to reduce nitrate-nitrogen content in ground water. Finally, once the soil profile becomes saturated, free water is easily perched above the fragipan, and is suspected to move down-slope laterally across the fragipan surface.

With regard to herbicides in runoff, losses were primarily dependent on the amount of runoff in the first runoff event after application and were independent of established tillage practice such as no-till, which reduced sediment loss by about two orders of magnitude compared to conventional tillage. Substantial herbicide losses (as much as 10-20%) resulted when 35 mm or more of runoff occurred within 1 w of broadcast (surface) applications of relatively water soluble herbicides such as metribuzin and metolachlor. With regard to herbicides in shallow ground water, the no-till practice provided a greater potential for herbicide leaching into the soil profile.

Ground water movement research indicated that matrix and preferential flow components were separated from total flow by a hydrograph-separation technique which used the assumption of dual porosity and a tracer mass balance. An estimate of the magnitude of water and Br⁻ transported by preferential flow to a drain line from irrigations applied by a rain simulator were shown in Figures 9 through 11. These hydrographs provide an indication of the potential significance of preferential flow in transporting water and chemicals that move like Br⁻ through macropores to the shallow groundwater system. These procedures should be considered a minimum estimate of the quantity of preferential flow due to the simplified assumptions of all preferential flow being intercepted directly by the drain and no dilution of tracer occurs in the preferential flow channels. Preferential flow in the drainage at any time was small as compared to the matrix flow, however it contributed a disproportionate amount of Br⁻ tracer. These data support the concept that models used to predict mass balances using only the matrix (Darcian) flow will thus underestimate those chemicals that move like bromide into the soil profile.

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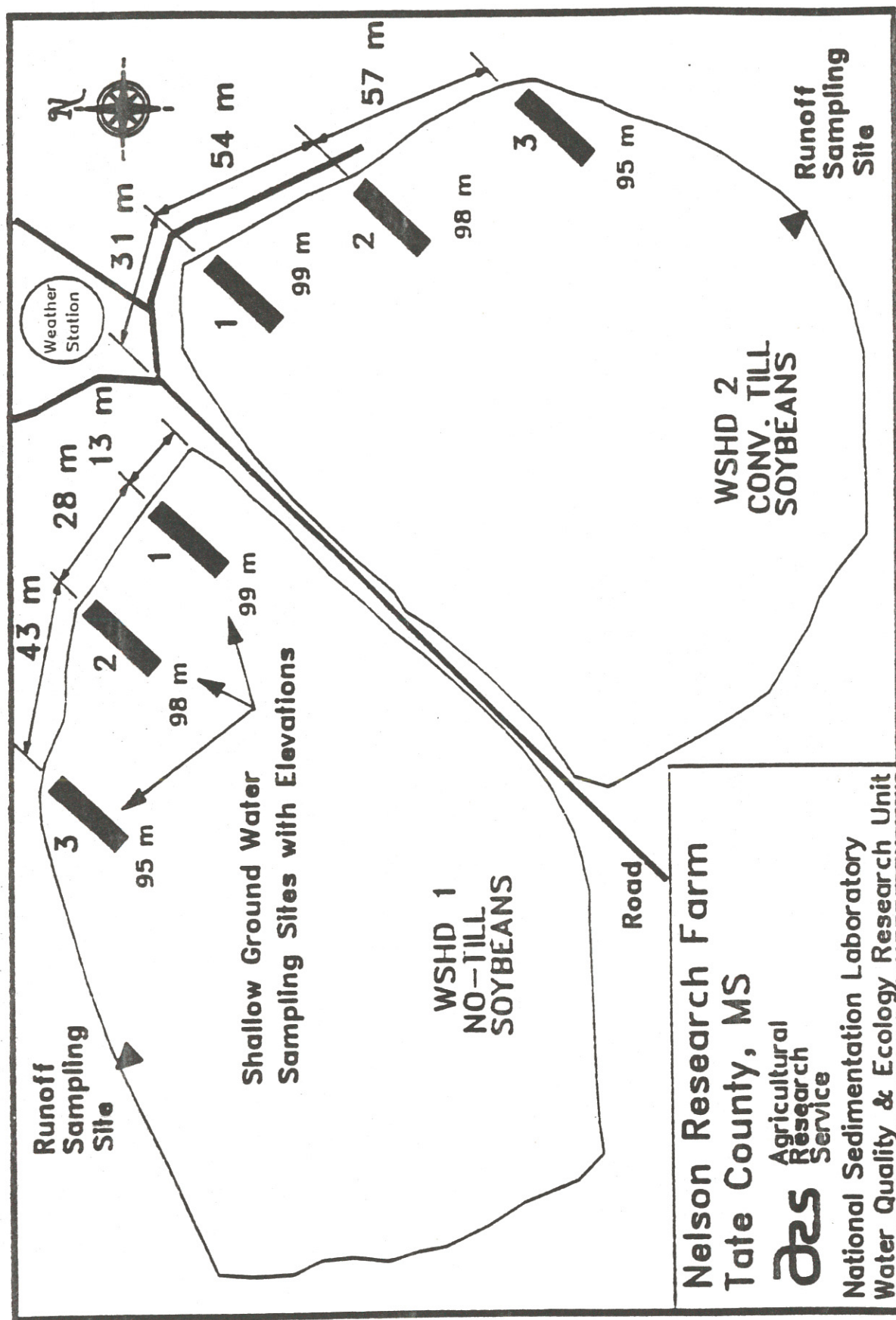
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VI. FIGURE CAPTIONS

- Figure 1. Location of runoff and ground water sampling sites.
- Figure 2. Nutrient concentrations in runoff from a no-till soybean watershed
- Figure 3. Nutrient concentrations in runoff from a conventional-till soybean watershed.
- Figure 4. Ground water in observation wells after a typical storm event.
- Figure 5. Nitrate-N concentrations in ground water of a no-till soybean watershed.
- Figure 6. Nitrate-N concentrations in ground water of a conventional-till soybean watershed.
- Figure 7. Basic structures and selected properties of herbicides found.
- Figure 8. Bromide concentrations (mg/L) in drain outflow of 5-hr rain event.
- Figure 9. Total drain flow rate (mL/min) with matrix and preferential flow components for undisturbed pasture, drilled drains.
- Figure 10. Total drain flow rate (mL/min) with matrix and preferential flow components for simulated-till, drilled drains.
- Figure 11. Preferential flow component as percentage of total outflow during first rain simulation.

VII. TABLES

- Table 1. Herbicide concentrations and losses in water phase of runoff from WSHD 1 (no-till) during the 1990 crop year.
- Table 2. Herbicide concentrations and losses in water phase of runoff from WSHD 1 (no-till) during the 1991 crop year.
- Table 3. Herbicide concentrations and losses in water phase of runoff from WSHD 2 (conventional-till) during the 1991 crop year.
- Table 4. Herbicide concentrations and losses in sediment phase of runoff from WSHD 2 (conventional-till) during the 1991 crop year.
- Table 5. Herbicide concentrations in shallow ground water in WSHD 1 (no-till) for crop year 1990.
- Table 6. Herbicide concentrations in shallow ground water in WSHD 1 (no-till) for crop year 1991.
- Table 7. Herbicide concentrations in shallow ground water in WSHD 2 (conventional-till) for crop year 1991.
- Table 8. Total discharge and total mass of Br- in drain outflow of each treatment.



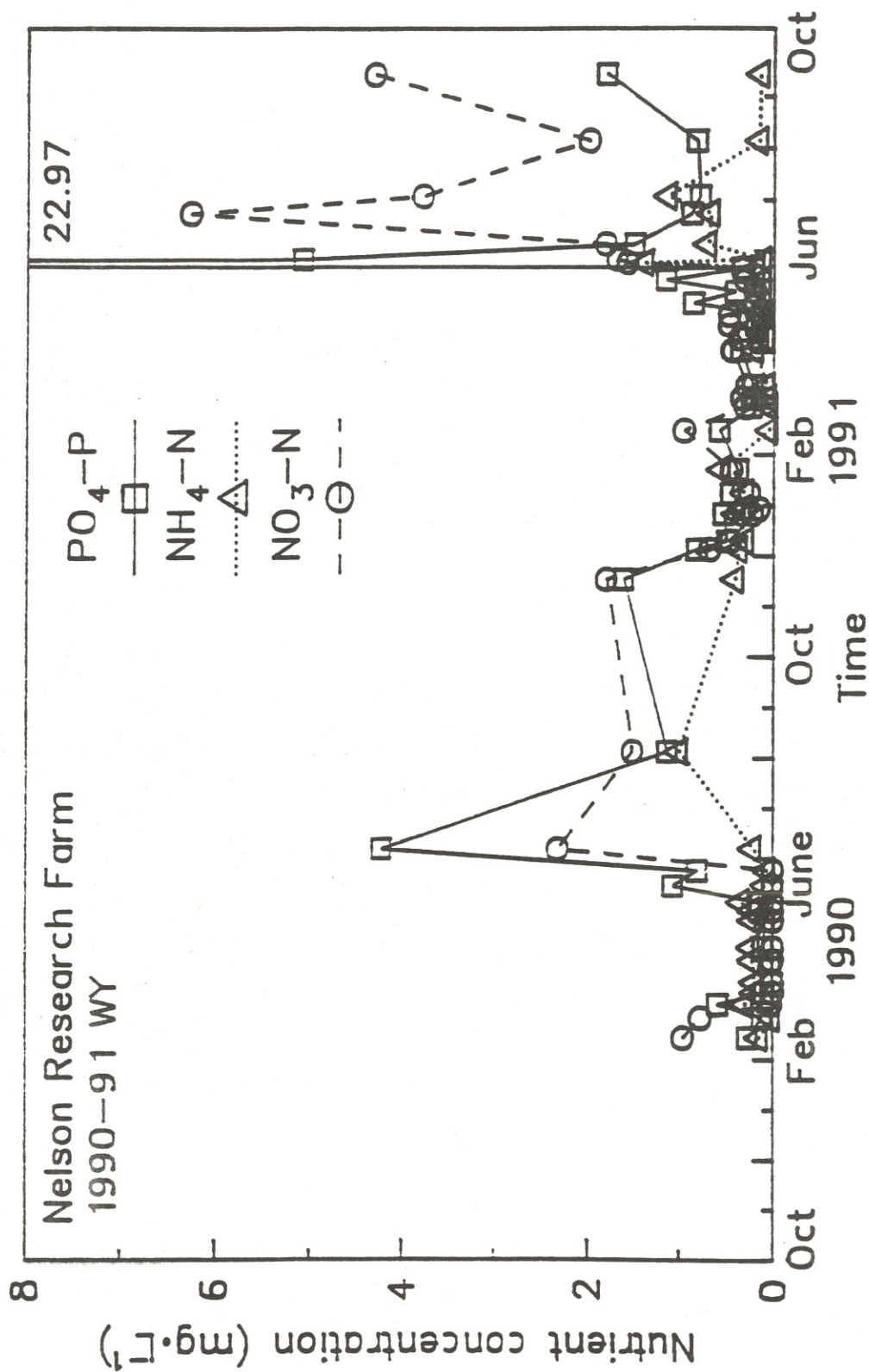


Figure 2. Nutrient concentrations in runoff from a no-till soybean watershed

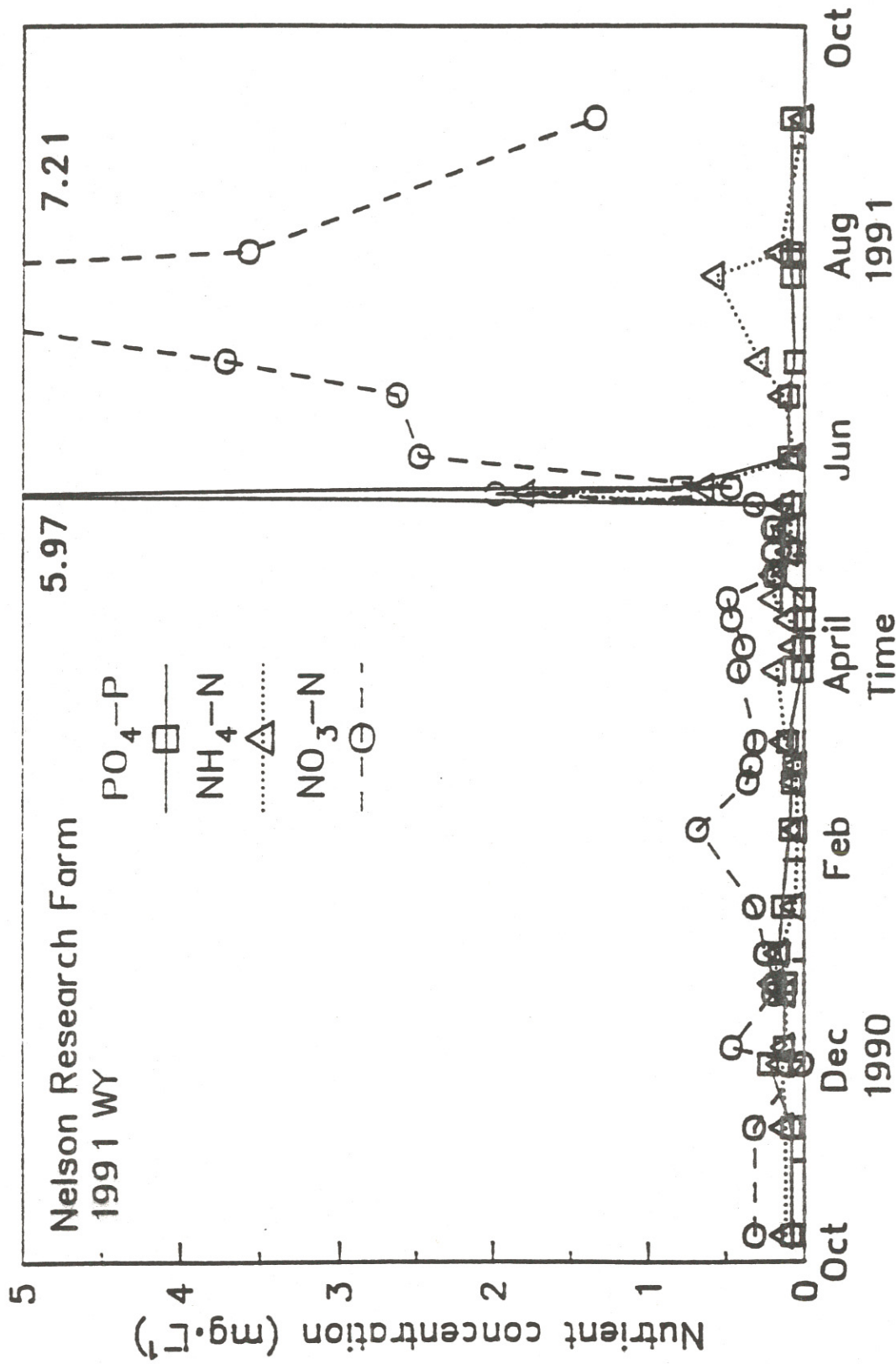


Figure 3. Nutrient concentrations in runoff from a conventional-till soybean watershed

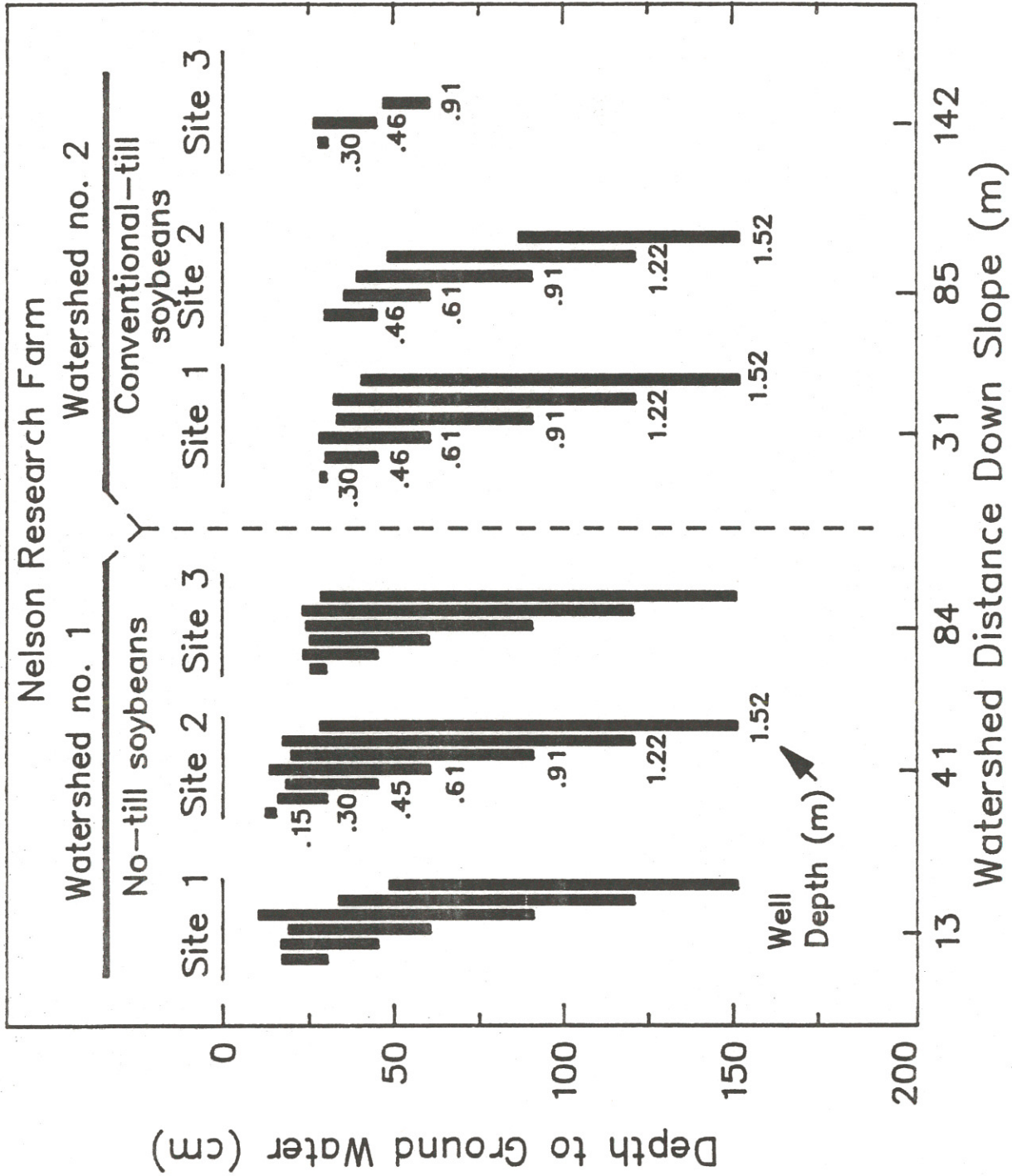


Figure 4. Ground water in observation wells after a typical storm event

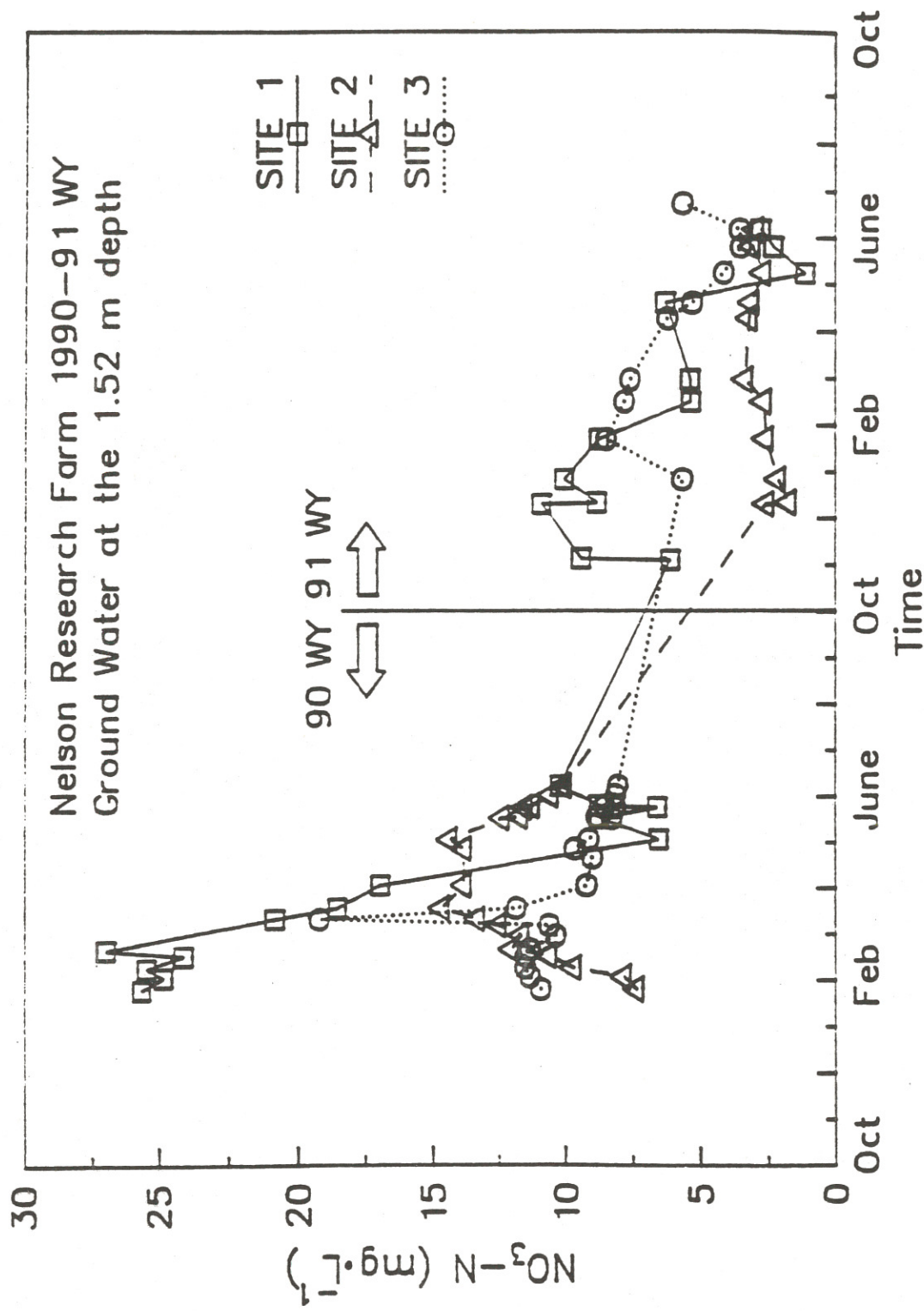


Figure 5. Nitrate-N concentrations in ground water of a no-till soybean watershed

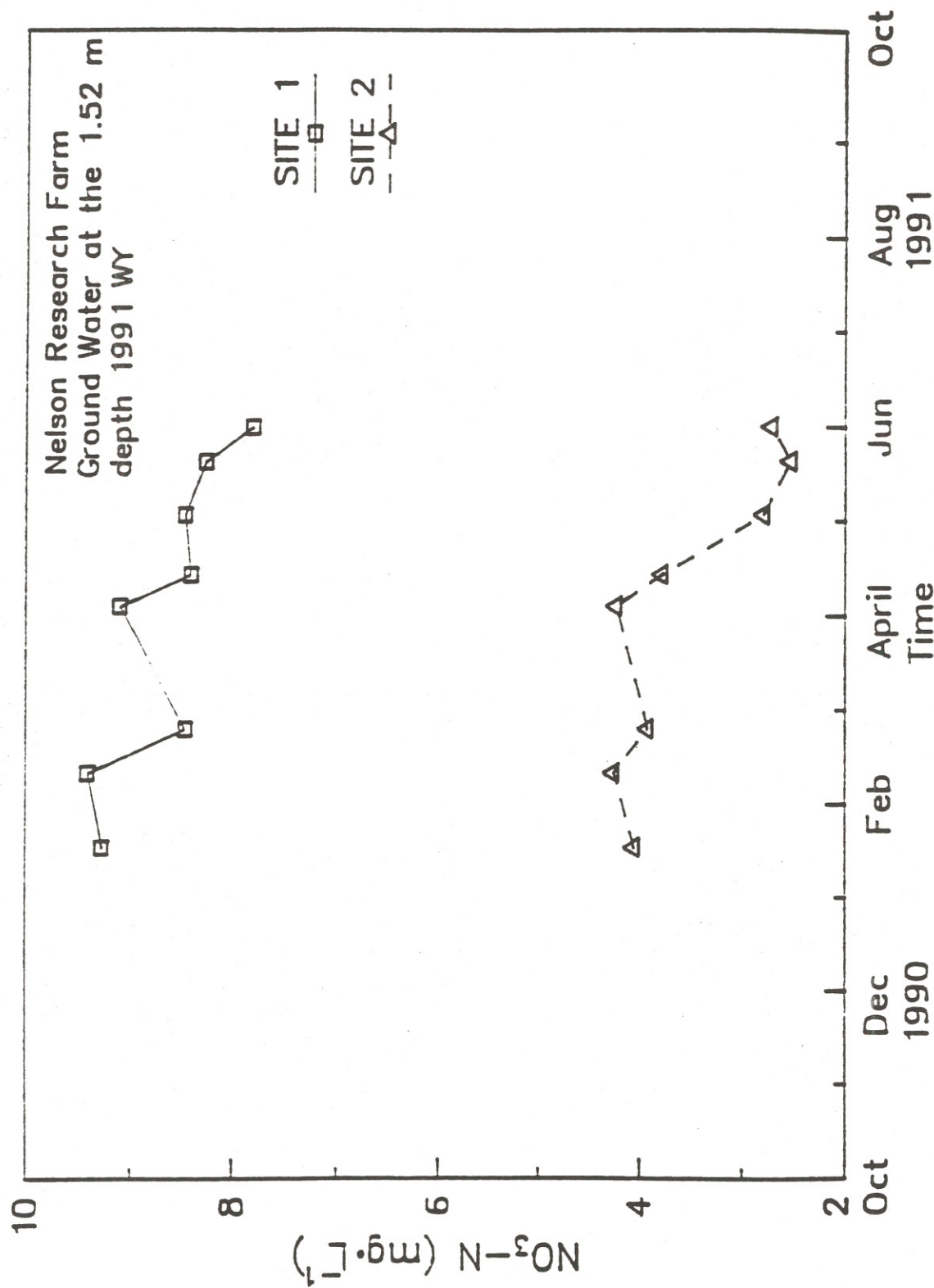
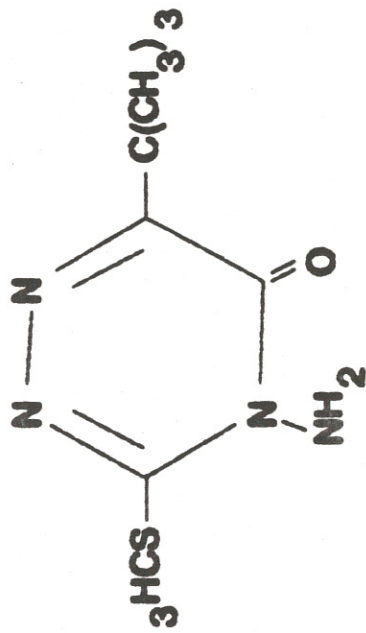


Figure 6. Nitrate-N concentrations in ground water of a conventional-till soybean watershed

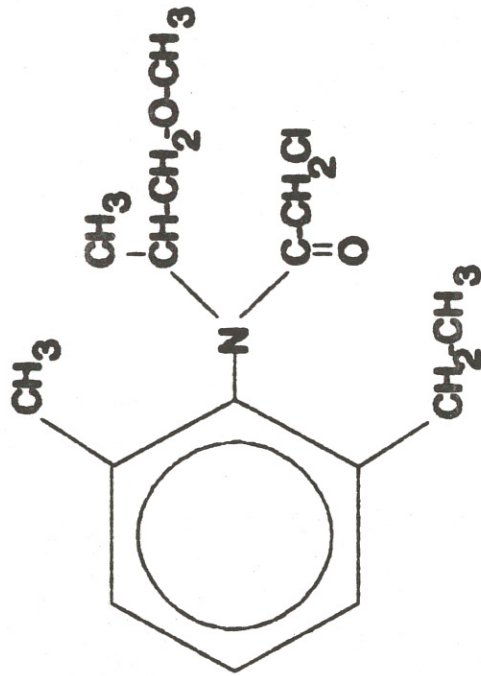


METRIBUZIN

$$S_{H_2O} = 1200 \text{ ppm}$$

$$K_{oc} = 24 \text{ cc/g}$$

$$t_{1/2} = 30-60 \text{ d}$$



METOLACHLOR

$$S_{H_2O} = 530 \text{ ppm}$$

$$K_{oc} = 181 \text{ cc/g}$$

$$t_{1/2} = 15-25 \text{ d}$$

Figure 7. Basic structures and selected properties of herbicides found.

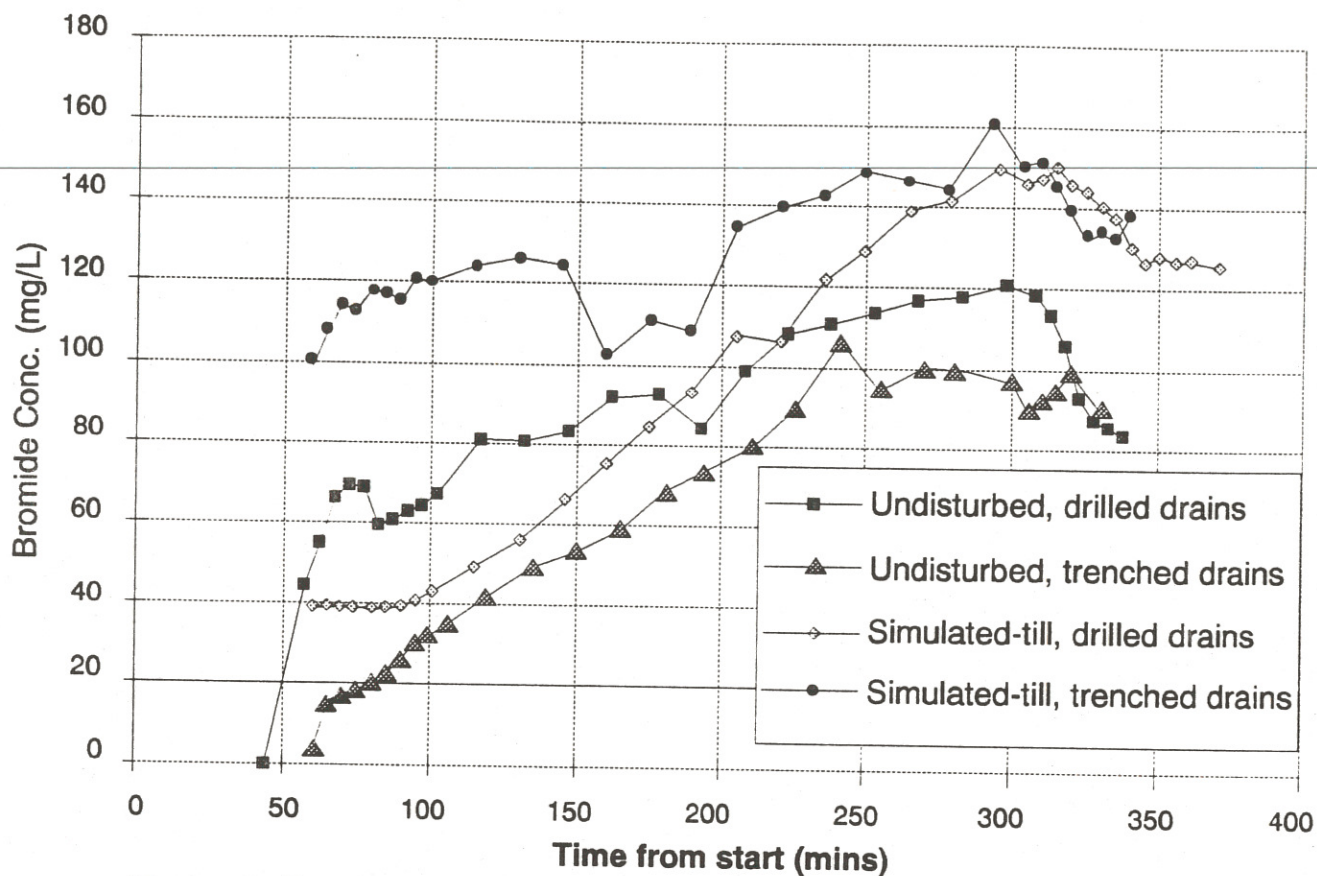


Figure 8. Bromide concentrations (mg/L) in drain outflow of 5-hr rain event.

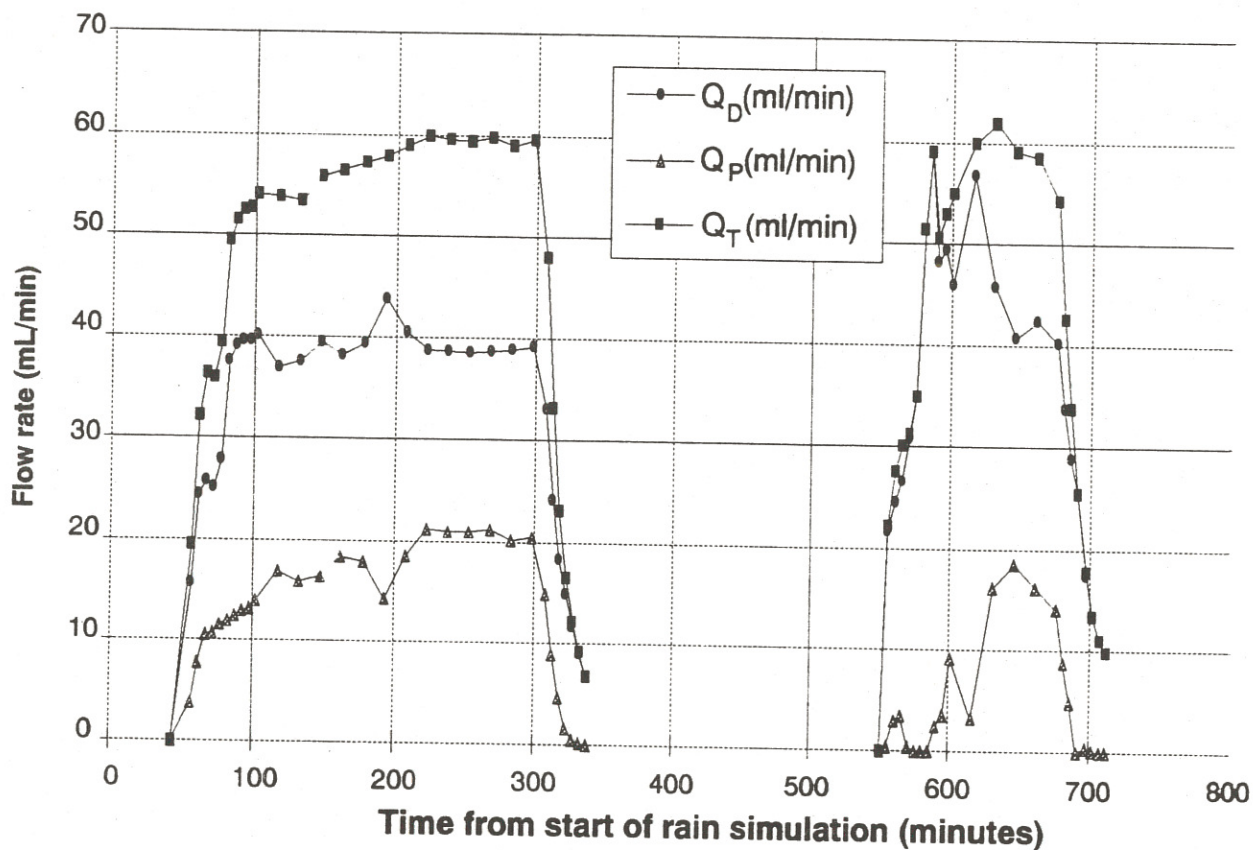


Figure 9. Total drain flow rate (mL/min) with matrix and preferential flow components for undisturbed pasture, drilled drains.

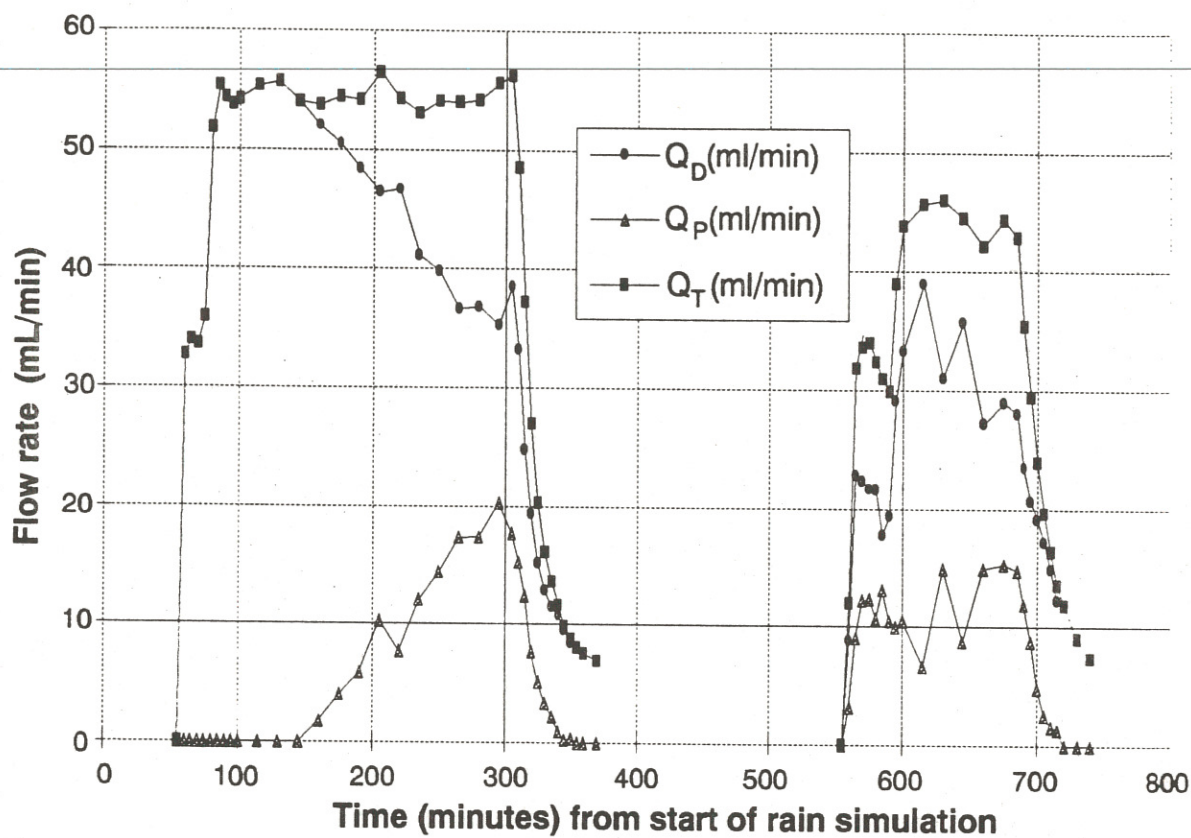


Figure 10. Total drain flow rate (mL/min) with matrix and preferential flow components for simulated-till, drilled drains.

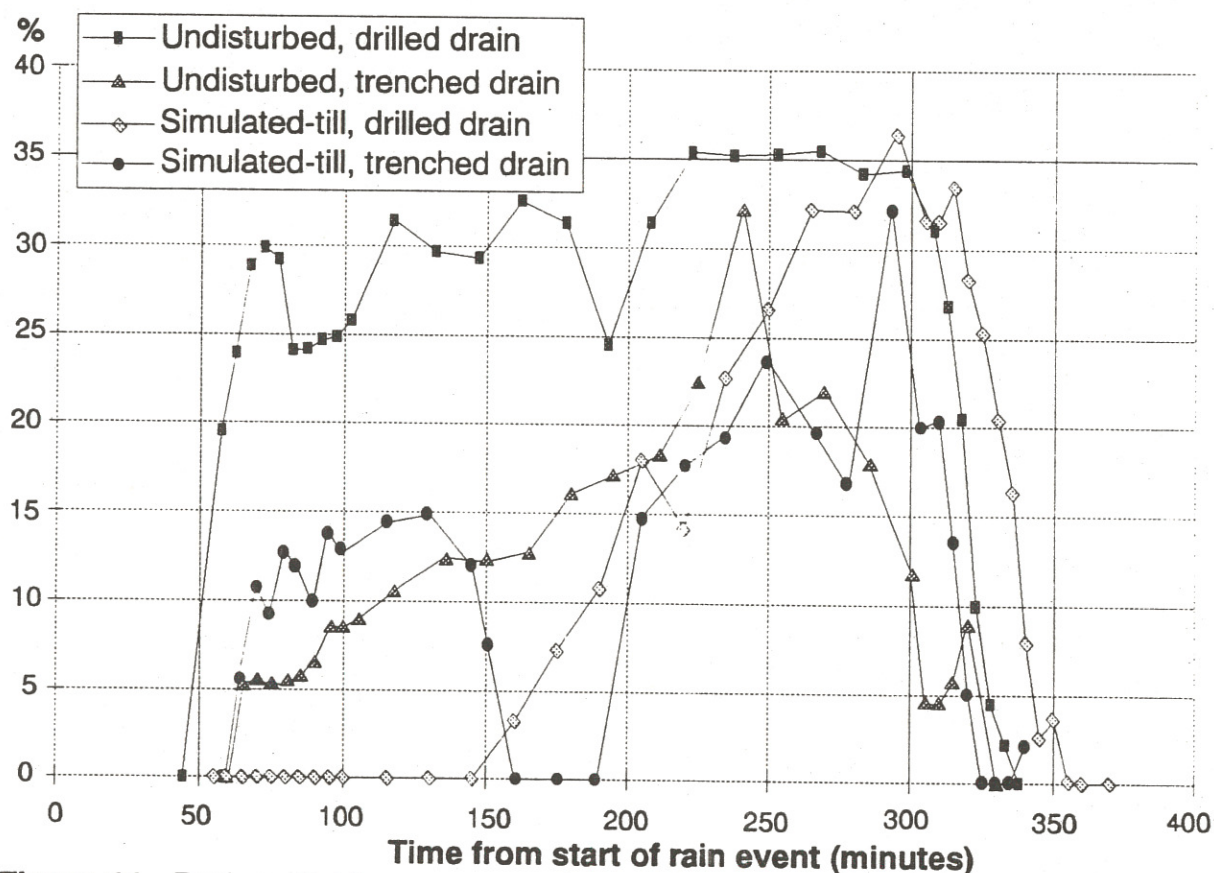


Figure 11. Preferential flow component as percentage of total outflow during first rain simulation.

Table 1

**Herbicide concentrations and losses in water phase of runoff
from WSHD 1 (no-till) during the 1990 crop year**

Sampling Date	Time after applic. days	Sed. conc. mg/L	Runoff mm	Metribuzin			Metolachlor		
				Conc. ppb	Loss g/ha	Loss % of applied	Conc. ppb	Loss g/ha	Loss % of applied
5/14/90	6	37	5.41	110.7	5.95	1.41	534.6	28.74	1.28
5/21/90	13	54	59.94	17.7	10.54	2.51	93.9	55.94	2.49
6/04/90	27	134	4.22	2.4	0.10	0.02	16.5	0.69	0.03
8/01/90	85	204	2.46	0.3	0.01	0.00	1.2	0.03	0.00
						3.94			3.80

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Table 2

**Herbicide concentrations and losses in water phase of runoff
from WSHD 1 (no-till) during the 1991 crop year**

Sampling Date	Time after applic. days	Sed. conc. mg/L	Runoff mm	Metribuzin			Metolachlor		
				Conc. ppb	Loss g/ha	Loss % of applied	Conc. ppb	Loss g/ha	Loss % of applied
5/27/91	5	204	35.94	223.2	79.78	18.96	524.8	187.56	8.36
6/14/91	23	551	21.74	11.0	2.38	0.54	24.9	5.38	0.24
7/26/91	64	143	3.71	1.2	0.04	0.01	2.4	0.09	0.00
9/03/91	103	154	2.18	0.0	0.00	0.00	0.0	0.00	0.00
						19.51			8.60


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Table 3

Herbicide concentrations and losses in water phase of runoff from WSHD 2 (conventional-till) during the 1991 crop year

Sampling Date	Time after applic. days	Sed. conc. mg/L	Runoff mm	Metribuzin			Metolachlor		
				Conc. ppb	Loss g/ha	Loss % of applied	Conc. ppb	Loss g/ha	Loss % of applied
5/27/91	4	20124	38.56	241.1	92.88	22.08	590.2	227.41	10.14
6/14/91	22	55055	26.24	10.2	2.69	0.64	70.4	18.45	0.82
7/26/91	63	42361	4.45	0.5	0.02	0.01	5.2	0.23	0.01
9/03/91	102	6957	5.69	0.2	0.01	0.00	0.9	0.05	0.00
						22.73			10.97


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Table 4

**Herbicide concentrations and losses in sediment phase of runoff
from WSHD 2 (conventional-till) during the 1991 crop year**

Sampling Date	Time after applic. days	Sed. conc. mg/L	Runoff mm	Metribuzin			Metolachlor		
				Conc. ppb	Loss g/ha	Loss % of applied	Conc. ppb	Loss g/ha	Loss % of applied
5/27/91	4	20124	38.56	90.1	0.70	0.17	312.4	2.42	0.11
6/14/91	22	55055	26.24	4.5	0.07	0.02	11.3	0.16	0.01
7/26/91	63	42361	4.45	1.2	0.00	0.00	11.2	0.02	0.00
9/03/91	102	6957	5.69	2.4	0.00	0.00	9.3	0.00	0.00
						0.19			0.12

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Table 5
Herbicide concentrations in shallow ground water
in WSHD 1 (no-till) for crop year 1990

		Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
			ppb						
5/14/90	Site								
	1	nw	nw	nw	nw	nw	nw	7.0	46.3
	2	nw	nw	nw	nw	nw	1.2	0.0	0.0
Metolachlor	3	nw	nw	nw	nw	nw	40.2	0.1	9.8
	1	nw	nw	nw	nw	nw	nw	11.8	72.0
	2	nw	nw	nw	nw	219.6	2.0	0.0	0.0
5/21/90	3	nw	nw	nw	nw	nw	270.0	1.1	28.4
	1	13.7	10.4	0.4	12.0	0.2	0.2	1.1	15.2
	2	13.8	0.5	9.2	21.4	8.3	0.0	0.0	0.1
Metolachlor	3	5.4	0.4	0.2	0.2	9.4	1.2	2.0	30.4
	1	45.7	26.6	1.0	28.0	0.0	2.3	0.0	0.0
	2	57.6	1.0	18.6	64.6	22.7	0.0	0.0	10.6
6/4/90	3	34.8	2.3	1.0	1.1	50.8	5.3		
	1	nw	nw	0.0	nw	0.1	0.6	3.6	
	2	nw	0.0	1.4	4.8	1.1	2.7	0.0	
Metolachlor	3	nw	nw	0.0	0.0	0.4	0.3	0.5	
	1	nw	nw	7.7	nw	0.5	1.6	8.5	
	2	nw	0.3	4.6	7.6	2.2	3.2	0.2	
	3	nw	nw	0.3	0.2	3.7	2.7	4.7	

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nw = no water in well

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Table 6

**Herbicide concentrations in shallow ground water
in WSHD 1 (no-till) for crop year 1991**

		Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
		ppb							
5/27/91	Site								
	Metribuzin 1	nw	nw	nw	nw	nw	2.0	49.5	151.4
	2	nw	nw	nw	nw	25.1	0.3	nw	2.1
	3	nw	nw	nw	nw	30.4	43.0	28.1	6.8
	Metolachlor 1	nw	nw	nw	nw	nw	1.4	82.2	254.0
	2	nw	nw	nw	nw	27.3	0.7	nw	3.1
6/14/91	3	nw	nw	nw	nw	72.3	68.2	36.5	10.7
	Metribuzin 1	nw	nw	11.5	nw	nw	0.8	10.6	nw
	2	nw	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	nw	4.4	4.4	0.7
	Metolachlor 1	nw	nw	22.3	nw	nw	1.3	26.5	nw
	2	nw	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	nw	13.1	7.0	1.5

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nw = no water in well

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Table 7

**Herbicide concentrations in shallow ground water
in WSHD 2 (conventional-till) for crop year 1991**

		Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
		ppb							
5/27/91	Site								
	Metribuzin	1	nw	nw	nw	nw	5.8	0.3	2.2
		2	nw	nw	nw	nw	4.1	0.0	7.5
		3	nw	2.2	0.9	0.5	nw	nw	nw
	Metolachlor	1	nw	nw	nw	nw	5.2	0.6	3.0
		2	nw	nw	nw	nw	3.9	0.4	8.2
6/14/91		3	nw	1.9	0.6	7.9	nw	nw	nw
	Metribuzin	1	nw	nw	nw	nw	nw	nw	nw
		2	nw	nw	nw	nw	nw	nw	nw
		3	nw	nw	nw	nw	nw	nw	nw
	Metolachlor	1	nw	nw	nw	nw	nw	nw	nw
		2	nw	nw	nw	nw	nw	nw	nw
		3	nw	nw	nw	nw	nw	nw	nw

Application date = 5/23/91

nw = no water in well

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Table 8. Total discharge and total mass of Br- in drain outflow of each treatment.

	5-Hour Storm			
	Undisturbed, Drilled Drain	Undisturbed, Trenched Drain	Simulated-Till, Drilled Drain	Simulated-Till, Trenched Drain
Discharge (V)				
Preferential (ml)	4,473	1,635	2,085	2,971
Total (ml)	14,586	10,477	14,361	21,034
% Preferential	30.6%	15.6%	14.5%	14.1%
Mass (C*V)				
Preferential (mg)	81	25	39	58
Total (mg)	118	61	121	242
% Preferential	69.0%	41.0%	32.1%	23.9%
3-Hour Storm				
Discharge (V)				
Preferential (ml)	1,206	1,162	1,667	1,355
Total (ml)	7,268	12,698	6,123	5,762
% Preferential	16.6%	9.2%	27.2%	23.5%
Mass (C*V)				
Preferential (mg)	16	28	44	33
Total (mg)	89	165	110	110
% Preferential	18.4%	17.1%	40.4%	29.8%

